

Performance Report :
**THE ROLE OF SEMICONDUCTING MINERALS IN THE PREBIOTIC
FIXATION OF NITROGEN AND CARBON**

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Background.

Biochemical compounds are made up largely of relatively reduced carbon and nitrogen. Today, these compounds are produced biogenically. Most theories for the origins of life depend on the synthesis of reduced carbon/nitrogen compounds from which self-replicating molecules (von Kiedrowski, 1986; Zeilinski et. al., 1987; Inoue et. al., 1984; Horowitz et. al., 1962; Eigen et. al., 1979; Kuhn et. al., 1981), membranes (Deamer et. al., 1980; Morowitz et. al., 1988; King, 1990; Deamer et. al., 1982; Koch, 1985), or surface metabolites (Wächtershäuser, 1988; Wächtershäuser, 1990; Drobner et. al., 1988; Wächtershäuser, 1988; Ingmanson et. al., 1977; Corliss et. al., 1981) can arise. Thus, abiotic sources of such compounds are crucial to such theories (Miller, 1974; Morowitz, 1992).

In a reducing atmosphere, electric discharges are sufficient for the fixation of both carbon and nitrogen (Stribling et. al., 1987; Chang et. al., 1983). However, geochemical evidence seems to point to a non-reducing atmosphere composed of CO_2 , N_2 , and H_2O (Chang et. al., 1983; Walker, 1985; Gregor et. al., 1988; Wood et. al., 1989; Kasting, 1987; Holland, 1989A). In such a neutral atmosphere, shock heating produces NO and CO (Kasting, 1990). Carbon dioxide and dinitrogen are relatively oxidized forms of carbon and nitrogen. They are also, especially for nitrogen, among the less reactive forms. Processes for the prebiotic synthesis of the "starting materials" of life need to accomplish two feats. One, supply a source of reducing equivalents. Two, overcome the low reactivity of carbon dioxide and dinitrogen.

One source of reducing equivalents is iron sulfide and iron oxide particles such as troilite (FeS) and magnetite (Fe_3O_4). Tectonic and/or volcanic activity was much higher on the early Earth than now (Windley, 1976; Turcotte, 1980). In addition, given much smaller or nonexistent continental masses (Windley, 1976; Windley, 1977), a greater proportion of this activity was in marine environments. Hydrothermal systems release large amounts of aqueous Fe^{+2} and H_2S . Most of the Fe^{+2} is precipitated, by the S^{-2} , as iron sulfides (Holland, 1973; Walker et. al., 1985; Drever, 1974; Veizer, 1978). Thus, one expects iron sulfide particles to be commonly associated with hydrothermal systems in the early ocean. Oxidation of aqueous Fe^{+2} , photochemical or otherwise (see below), would produce Fe_3O_4 . Since both magnetite and troilite contain divalent iron, Fe(II)/Fe(III) represents a redox couple capable of supplying reducing equivalents to reactions being catalyzed on the surface of such particles. The redox capacity of prebiotic oceans, the primary source of Fe(II) , would far outweigh that of the atmosphere and would have been continually replenished by volcanic activity (Wolery et. al., 1976; Veizer, 1983; Cloud, 1973).

Additionally, semiconducting particles represent a second source of reducing equivalents. When in contact with a solution, the bands of a semiconductor will bend to bring the fermi level to the redox level of the solution (Morrison, 1980; Morrison, 1977). When illuminated, electrons are excited into the valence band, leaving vacancies (holes) in the conduction band where the electrons were. For a p-type semiconductor, the electrons are driven to the surface. The energy difference

between where the electrons arrive at the surface, and the fermi level, is the amount of extra reducing power available from illumination (the photovoltage). In a reverse manner, n-type semiconductors show an increased oxidizing power. When appropriately sized semiconducting particles are illuminated, holes and electrons in the same particle can be driven to the surface separately (M. Graetzel, 1983; Bard, 1979; Yesodhara et. al., 1983) to drive electrochemical reactions that will not proceed thermally. The amount of photoelectrochemical energy, namely the photovoltage, available to drive such reactions depends, in part, on the amount of energy used to excite an electron from the valence band to the conduction band (the band gap).

Many iron sulfides (for example, pyrite) and iron oxides (for example, hematite) are semiconducting (Finlea, 1988; S. Sakkopoulos, 1986; Mishra, 1988; Lalvani et. al., 1990; Danielewski et. al., 1980). On the early Earth, high levels of volcanic activity would have yielded abundant iron sulfide particles in and around hydrothermal systems (see above). Also, the geological context of the first compelling evidence of life indicates conditions dominated by island volcanism and hydrothermal activity in a shallow marine environment (Barley et. al., 1979; Groves et. al., 1981). This indicates that iron sulfide particles suspended in shallow waters, or deposited in shallow or tidal sands, may have been relatively common on the early Earth.

Reducing power only indicates the thermodynamic ability to drive a reaction. It does not prove that the reaction will go at a significant rate. However, in addition to providing energy transduction, semiconducting particles can provide catalytic surfaces for reactions. For example, it has been shown that GaAs electrodes will catalyze the electroreduction of carbon dioxide all the way to methanol (Canfield et. al., 1983). It has been shown (see below) that FeS particles have activity toward nitrite reduction.

While the electrochemical reduction of dinitrogen is not thermodynamically difficult, it has proven kinetically to be nearly intractable. Additionally, the solubility of dinitrogen in water is not significant. Titanium oxide particles in desert sands will reduce gaseous nitrogen to ammonia (Schrauzer et. al., 1983). However, the amount of subaerial land surface area on the early Earth is questionable, especially because land masses were probably scarce or non-existent (Windley, 1977; . Windley, 1976b). There are no examples of such reduction under aqueous conditions. However, shock heating in the atmosphere can solve part of our problem. In a N_2/CO_2 atmosphere shock heating will produce NO (Kasting, 1990; Chameides et. al., 1981; Yung et. al., 1979; Kasting et. al., 1990; Mancinelli et. al., 1988). The NO would react with photochemically-generated HCO to produce HNO (Mancinelli et. al., 1988). HNO is soluble and would be rained into the oceans. In the ocean NO^- , from the dissociation of HNO, can either disproportionate, or react with NO to form N_2O , NO_2^- , NO_3^- . Thus we can consider methods to reduce nitrate and nitrite, both of which are soluble and more reactive than dinitrogen.

Kinetically, the direct reduction of carbon dioxide is a fairly tractable problem compared to the reduction of dinitrogen. Carbon dioxide has good solubility in aqueous solution. The

electrochemical reduction at poorly catalytic surfaces tends to lead to formic acid as a product and requires large overvoltages (additional voltage, past what is needed thermodynamically, applied to increase the rate) to get good rates (Paik et. al., 1969; Russell et. al., 1977; Kapusta et. al., 1983; Teeter et. al., 1954; Ito et. al., 1975; Udupa et. al., 1971). At catalytic surfaces, carbon dioxide has been reduced to carbon monoxide, methanol, and methane (Summers et. al., 1986; Frese et. al., 1988; Summers et. al., 1988; Kim et. al., 1988; Summers et. al., 1988). Semiconductor electrodes have been shown to reduce carbon dioxide to carbon monoxide, formaldehyde, formic acid, and methanol (Canfield et. al., 1983).

Other semiconducting minerals have been shown to photoreduce carbon dioxide to formaldehyde (Halmann et. al., 1981). In addition to several minerals of exceedingly low geochemical abundance, iron rich clays, whose abundance on the early Earth is hard to predict, were studied. In the latter case the kinetics of the reduction were not studied, nor was the effect of environmental factors (see below) considered (Halmann et. al., 1981). Also, the pH's were probably below 4 (The actual pH's were not reported but reactions were run in a carbon dioxide saturated aqueous suspension. The pH of a carbon dioxide saturated aqueous solution with no added bicarbonate, or other source of alkalinity, is ~3.9.) which would be too low for most estimates of early oceanic pH's (Walker, 1983). It has also been reported that aqueous Fe^{+2} will photoreduce carbon dioxide to formaldehyde at pH 3 (Akermark et. al., 1980). Again, this pH is too low for estimates of pH in the early ocean (Walker, 1983). Reports of aqueous Fe^{+2} photoreduction of carbon dioxide at pH 6.3-7.5 (Finlea, 1988) have been retracted (Borowska et. al., 1992). It has been reported that FeCO_3 will reduce carbonate to "organic compounds" (Joe et. al., 1986). However, no experimental details, kinetics, or product identification are provided.

An opportunity arises if one semiconductor can be found to reduce both carbon dioxide and nitrite/nitrate under the same conditions. Under such conditions it is possible that carbon and nitrogen containing intermediates may combine on the surface to produce carbon-nitrogen compounds. For example, combination of S-CH and S-N, both intermediates in carbon dioxide and nitrogen reduction, where S=surface (Weatherbee et. al., 1982; Summers et. al., 1988; M. Boudart et. al., 1984; Morikawa et. al., 1971), may produce HCN.

Another issue that needs to be addressed is the importance of environmental factors on the reactions in question. The temperature of the early ocean at the time of life's origin is unknown and would probably have varied significantly over the surface of the planet and possibly over time (Ernst et. al., 1983). The pH of the oceans is likely to have ranged anywhere from 6 to 8 (Walker, 1983). While the composition of sea water on the early Earth is not known, it almost certainly was not pure water and contained dissolved salts as it does today. Such species may promote or poison reactions. In particular, anionic species may bind to the surface and block catalytic sites. Higher concentrations of carbon dioxide, and related concentrations of bicarbonate, are also factors that need to be addressed. To be useful for theories on the origins and evolution of life any study will

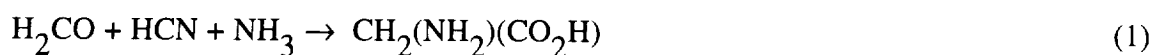
have to consider and address such factors.

Conversely, how reactions work under different sets of conditions is also important in evaluating the importance of those reactions on the early Earth. Kinetic data, and analysis and modeling of such data, in the context of the organic geochemistry and chemical evolution of early seawater, will have implications in the evaluation of various formation processes. Such analysis is crucial to understanding how such processes fit into an over-all understanding of the origin of life.

A final question of importance is, how will the routes outlined above for carbon and nitrogen fixation lead into subsequent steps in the origin of life? Fixation of nitrogen is one in a series of separate processes, each of which is interlinked with the next (similar to natural systems today). The products of fixation need to be combined to form more complex species necessary for proto-cellular structure, information storage/transference, etc.. Finally, all this needed to be combined to form a "proto-metabolism" for the first organism.

To make the study of the origin of life tractable, such steps are often broken down into individual problems which are then studied independently. However, regardless of what reservoirs or concentration mechanisms may have been in existence, in general reactions had to occur in the same place and under the same conditions (ie. the origin of life is a "one-pot synthesis"). How will these reactions interact with each other? Do they interfere with each other? Can they occur under the same (prebiotically plausible) conditions?

One such situation is the use of ammonia from the reduction of nitrite to ammonia in the Strecker Synthesis, reaction 1 (March 1985; Chang 1993). However, as discussed above, both reactions need



to occur together. What effect will the presence of Fe(II) have on the Strecker synthesis? What effect will CN^- have on the reduction of NO_2^- to NH_3 by Fe(II)? Will complexation of the cyanide to the iron deactivate one or the other (or both)? Will both of the reactions proceed under the same conditions? Conversely, could a $\text{Fe}(\text{CN})_n^{+(2-n)}$ type species provide some beneficial effect, either for the reduction of nitrite/nitrate or for the formation of amino acids?

The oxidation state of prebiotic environments is uncertain. We need to be able to show how fixation of nitrogen and carbon could have occurred under all oxidation states permitted by available evidence. If we can establish viable abiotic routes for the fixation of carbon and nitrogen in a prebiotic environment containing a neutral (non-reducing) atmosphere we will have extended our ability to understand how life might have originated under such conditions. Then theories on the origin of life need not be tied down to one set of environmental/geochemical conditions necessary for any individual source of fixed nitrogen/carbon. The objectives of this work do not address the issues surrounding endogenous formation of organic material vs exogenous delivery

(Chyba et. al., 1992). However, such a comparison can not be made until the available pathways and rates of endogenous formation are better understood. Also, such processes are important for an understanding of the early geochemistry of the early Earth and perhaps also other planets.

Results.

REDUCTION OF CARBON DIOXIDE.

Colloidal suspensions of FeS and FeS₂ were irradiated under 1 atm of carbon dioxide at pH's of 4 to 7.6. (pH > 7.6 can't be reached under 1 atm carbon dioxide because of the limitations of sodium bicarbonate solubility) Because of the shift of band edges to higher energy, quartz tubes were used as reaction vessels. After irradiation for 2-3 days, the samples were analyzed for formic acid and/or formaldehyde. Under most conditions, no evidence for carbon dioxide reduction was observed. Irradiation of pyrite at pH 7.6 did produce levels of formate that were slightly above background (0.2 ppm vs 0.06 ppm). This increased level could be real, or it could be due to variations in the the formate background of unknown cause.

Irradiation of pyrite at pH 4 produced Fe₂O₃, but no formaldehyde or formic acid. The formation of hematite occurs by the sacrificial photooxidation of the iron in pyrite. This raises the question of what species was reduced. A likely possibility is disproportionation of the pyrite which is consistent with the lack of formate and formaldehyde. Another possibility is the reduction of either water or carbon dioxide to hydrogen or carbon monoxide respectively.

In the time remaining in the period, the experiment at pH 4 will be checked for the formation of hydrogen or carbon monoxide. Additionally, the formation of format at pH 7.6 will be also be checked by the use of C¹³. In a typical experiment, a colloidal suspension will be prepared under nitrogen as previously described (see above). Under nitrogen, the appropriate amount of Na₂C¹³O₃ will be added. Then the tube will be evacuated and an appropriate amount of HCl will be injected. Enough carbonate and acid will be used so that the final pH and partial pressure of carbon dioxide are 7.6 and 0.8 atm respectively. The sample will be irradiated with a medium pressure mercury arc lamp in a quartz vessel. Then the carbonate will be neutralized with a minimum of HCl and purged with nitrogen to remove unreacted carbon dioxide (formic acid has a boiling point almost identical to water so loss of formic acid will not be a problem). The solution will then be made strong alkaline and the water is distilled off (as long the solution is kept at room temperature, loss of ammonium formate is not a problem). The ammonia formate residue will then be treated with a derivitizing agent (N-Methyl-N-t-Butyldimethylsilyl Trifluoroacetamide with 1% t-Butyldimethylchlorosilane) and analyzed by GC-MS. The procedure will be checked with unlabeled carbonate and authentic sample of formate first to make sure that C¹³ isn't wasted.

REDUCTION OF NITROGEN.

Nitrite Reduction and the Strecker Synthesis.

Work on the compatibility of the reduction of nitrite to ammonia by iron(II) and the Strecker

synthesis was also carried out. The questions of whether the production of ammonia by nitrite reduction by Fe(II) can feed into the Strecker, or cyanide interferes with nitrite reduction and/or iron interferes with the Strecker synthesis was addressed.

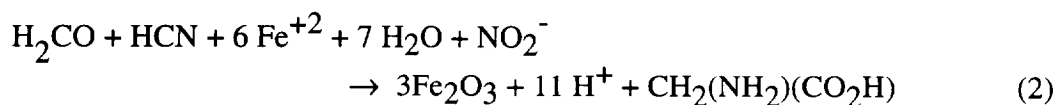
The formation of ammonia from the reduction of nitrite by Fe^{+2} was compared with nitrite reduction by $\text{Fe}(\text{CN})_6^{-4}$. A typical experiment involved stirring 20 mM NaNO_2 and 16 mM $\text{KFe}(\text{CN})_6$ at room temperature, pH 8, and under nitrogen for 3 days followed by analysis for ammonia and nitrite by ion chromatography. No ammonia was detected indicating that complete complexation of Fe^{+2} prevents nitrite reduction. Lowering the pH, to protonate cyanide ions and make them unavailable for binding to iron, doesn't help until the reaction mixture is too acidic for ammonia formation (Summers et. al., 1993).

The formation of ammonia by Fe^{+2} in presence of different amounts of added cyanide was also studied. In a typical experiment 12 mM of FeCl_2 and 0.32 M NaNO_2^- was stirred under nitrogen at pH 8 and room temperature and analysed for ammonia after 2 hours and 24 hours. When a cyanide/iron ration was less than 4:1, ammonia is formed. As the cyanide/iron ration increases over the 0:1 to 4:1 range, a steady decrease in the product distribution away from ammonia is observed. At ratios of less than 2:1, the effect is small. At cyanide/iron ratios of 4:1, or greater, ammonia is not formed. At a ratio of 4:1 we get to a $\text{Fe}[\text{Fe}(\text{CN})_6]_2^{-6}$ where two $\text{Fe}(\text{CN})_6^{-4}$ can bind facially to a Fe^{+2} . This completely blocks coordination of the Fe^{+2} and prevent reduction of nitrite.

The formation of ammonia from nitrite in the presence of cyanide doesn't appear to be a problem on the early Earth. Cyanide would be formed in the atmosphere (Bar-Nun et. al.; Zahnle; Wen et. al.) and rained into the oceans (which the presence of banded iron formations indicate were iron rich, Holland, 1973; Walker et. al. 1985; Derry et. al.; Holland, 1989B). The situation was one where cyanide was essentially being "titrated" into an ocean with excess quantities of iron. This implies cyanide/iron ratios of less than 1:1. Under such conditions, the change in the reduction of nitrite to ammonia is small.

Work also focused on the question of whether the Strecker synthesis can be carried out in the presence of iron(II). Typical experiments consisted of following the formation of glycine, iminodiacetic acid, and glycolic acid as a function of time. The reaction mixture consisted of; cyanide, formaldehyde, and ammonia (either at 0.1 M or 0.1 mM) in the presence of different amounts of added Fe^{+2} . The presence of iron in almost any quantity, up to a 10 fold excess, does not interfere with the formation of glycine. The formation of glycolic acid, a side product, is also unaffected. The formation of iminodiacetic acid (another side product) appears to be decreased by the presence of iron, but only in more concentrated solutions. This may be due to a larger fraction of the glycine formed in the reaction being complexed at higher ferrous iron concentrations, preventing it from reacting further to form iminodiacetic acid. It appears that the Strecker synthesis has little sensitivity toward whether the cyanide it uses is free or bound to a metal center.

Finally, the actual combination of the nitrite reduction and the Strecker synthesis in the formation of amino acids (reaction 2) was demonstrated. A reaction mixture of nitrite, iron(II) (Fe^{+2} or



FeS), cyanide, and formaldehyde formed glycine and iminodiacetic acid at levels comparable to control reactions using ammonia.

Sources and Sinks for Nitrite and Ammonia.

An analysis of the sinks and sources of nitrite and ammonia was conducted. In addition to providing a more detailed analysis than had been presented in earlier papers (Summers et. al., 1993), the analysis also addressed the impact of the reaction of nitrite with ammonia (ie with it's own reduction product, Rubin et. al., 1987) on the importance of nitrite reduction as a source of reduced nitrogen. It had been claimed that such "back reaction" of nitrite and ammonia means that the formation of ammonia from nitrite could not have been an important prebiotic source of ammonia.

At 25 °C, pH 7.6, and 0.2 atm CO_2 , it was determined that the most significant sink for nitrite is reduction by Fe^{+2} to ammonia. The reduction is slightly slower than the rate of mixing between the upper layer and the deeper portions of the ocean so steady state nitrite concentrations are the same in both layers. Destruction at hydrothermal vents and back reaction with ammonia are both not significant (esp. back reaction). Photochemical destruction, as a "worst case", is possibly important.

From 5 °C to 100 °C, the predominate sink for nitrite was again found to be reduction by ferrous iron. As the temperature increases, the rate of reduction increases and the steady state concentration of nitrite begins to drop, first in the lower depths as more and more nitrite is reduced before it can be mixed down, and then at the surface. Below 5°C, the nitrite concentration at depth is high enough that destruction in hydrothermal systems is the predominate sink for nitrite. The rate of back reaction is less temperature dependant than the rate of reduction and it's relative importance as a sink declines with increasing temperature. Hydrothermal destruction begins to fall as soon as steady state concentrations in deeper waters decrease. Worst case photolysis drops as the steady state concentration in near surface waters decreases, becoming less important than reduction regardless of conditions.

The concentration of Fe^{+2} is inversely proportional, because it is fixed by solubility of $\text{Fe}(\text{CO}_3)$, to the carbon dioxide partial pressure. Reduction of nitrite was found to be fast enough, to at least a carbon dioxide partial pressure of 1 atm, to remain the most significant sink for nitrite. At partial pressures greater than 0.01 atm, worst case photolytic destruction could be important. Other sinks, esp. back reaction, remain unimportant at all pressures. Below a partial pressure of

~0.3 atm, the rate of reduction is fast enough to deplete the lower levels of the ocean in nitrite.

The reduction of nitrite falls off sharply below pH 7.3 (Summers et. al., 1993). Below this value destruction at hydrothermal vents were found to be the predominate sink. Worst case photochemical destruction is also a possibly significant sink. As the pH increases above 7.6 (the maximum for nitrite reduction) the rate of reduction falls off. Above pH 7.3, reduction is the primary sink until ~8.5 when the destruction of nitrite in hydrothermal systems becomes more important. The worst case for photolysis indicates that this sink may also be important. In all cases, back reaction doesn't appear to be an important sink.

At 25 °C, pH 7.6, and 0.2 atm CO₂, the primary sink for ammonia was determined to be photochemical destruction in the atmosphere. For ammonia, sinks are slower than mixing between the upper and lower layers of the ocean. Destruction in the atmosphere remains the primary sink at all temperatures. Back reaction is the least important sink. At different partial pressures of carbon dioxide, the most important sink is also photochemical destruction. The rate of back reaction doesn't vary but, because the concentration of nitrite decreases as CO₂ partial pressure decreases, so does the importance of the sink.

The formation of ammonia was extrapolated to more acidic conditions to illustrate how pH might affect various sinks and the ammonia concentration. Over pH's that reduction by Fe⁺² occurs, the primary sink is again photochemical destruction. Destruction at hydrothermal vents and by back reaction is unimportant. At acidic pH's, photochemical destruction in the atmosphere falls off as more the ammonia is present as NH₄⁺ and less NH₃ equilibrates into the atmosphere to be destroyed. Eventually the rate of destruction by hydrothermal vents become more important than photolysis.

Thus, under most conditions, the primary fate of nitrite was found to be reduction to ammonia. The primary sink for ammonia was found to be photochemical destruction in the atmosphere. At 25 °C, pH 7.6, and 0.2 atm CO₂ nitrite and ammonia have steady state concentrations of 3×10^{-8} M and 2×10^{-6} M respectively. In all cases reaction of ammonia with nitrite does not appear to be an important process.

References.

- Akermark, B., Eklund-Westlin, U., Baeckström, P., & Löf, R.: 1980, *Acta Chemica Scandinavica B* 34,27-30.
- Bar-Nun, A and Chang, S.: 1983, *J. Geophysical Research* 88,6662-6672.
- Bard, A. J.: 1979, *J. Photochem.* 10,59-75.
- Barley, M. E., Dunlop, J. S. R., Glover, J. E., & Groves, D. I.: 1979, *Earth and Plant. Sci. Lett.* 43,74.
- Bergmeyer H. U. (ed): 1974, *Methods of Enzymatic Analysis*, Academic Press, p 1551.
- Borowska, Z. & Mauzerall, D.: 1992, *Origins of Life.*
- Borowska, Z. & Mauzerall, D.: 1988, *Proc. Natl. Acad. Sci. USA* 85,6577-6580.
- Boudart, M. & Djega-Mariadassou, G.: 1984, *Kinetics of Heterogenous Catalytic Reactions*, Princeton University

Press.

- Brateman, P. S., Cairns-Smith, A. G., & Sloper R. W.: 1983, *Nature* 303,163.
- Canfield, D. & Frese, K. W.: 1983, *J. Electrochem. Soc.* 130,1772-1773.
- Canuto, V. M., Levine, J. S., Augustsson, T. R., Imhoff, C. L., & Giampapa, M. S.: 1983, *Nature* 305,281-286.
- Cairns-Smith A. G.: 1978, *Nature* 276,807.
- Chameides, W. L. and Walker, J. C. G.: 1981, *Origins of Life* 11,291-302.
- Chang S.: 1993, in *The Chemistry of Life's Origins*, Kluwer Academic Press, Dordrecht Netherlands, 279-282.
- Chang, S., Des Marais, D., Mack, R., Miller, S. L., & Strathearn, G. E.: 1983, *Earth's Earliest Biosphere* (ed. J. W. Schopf), Princeton University Press, p53-92.
- Chyba, C. & Sagan, K.: 1992, *Nature* 355,125-132.
- Cloud, P.: 1973, *Economic Geology* 68,1135..
- Corliss, J. B., Baross, A. J. & Hoffman, S. E.: 1981, *Oceanologica Acta* 5P,59-59.
- Danielewski, M., Mrowec, S., & Stoklosa, A.: 1980, *Solid State Ionics* 1,287-309.
- Deamer, D. W. & Oro, J.: 1980, *Biosystems* 12,167-175.
- Deamer, D. W. & Barchfield, G. L.: 1982, *J. Mol. Evol.* 18,203-206.
- Derry, L. A. & Jacobsen, S. B.: 1990, *Geochemica et Cosmochemica Acta* 54, 2965-2975.
- Drever, J. I.: 1974, *Geological Soc. Amer. Bull.* 85,1099-1106.
- Drobner, E., Huber, H., Wächtershäuser, G., Rose, D., & Stetter, K. O.: 1988, *Nature*, 346,742-744.
- Eigen, M. & Schuster, P.: 1979, *The Hypercycle*, Springer, Berlin.
- Ernst, W. G.: 1983, *Earth's Earliest Biosphere: It's Origin and Evolution* (ed J. W. Schopf), Princeton Univ. Press, p49-52.
- Finlea, H. J.: 1988, *Semiconductor Electrodes*, Elsevier, p147-199.
- Frese Jr., K. W. & Summers, D. P.: 1988, *Catalytic Activation of Carbon Dioxide*, ACS Symposium Series No. 363 (ed W. M. Ayers), American Chemical Society, p155-170.
- Graetzel, M. (ed.): 1983, *Energy Resources Through Photochemistry and Catalysis*, Academic Press, New York.
- Gregor, C. B., Garrels, R. M., Mackenzie, F. T., & Maynard, J. B. (eds): 1988, *Chemical Cycles in the Evolution of the Earth*, John Wiley & Sons.
- Groves, D. I., Dunlop, J. S. R., & Buick, R.: 1981, *Scientific American* 245,64.
- Halmann, M. Aurian-Blajeni, B. Bloch, S.: 1981, *Origin of Life* (ed Y. Wolman), D. Reidel Publ. Comp., New York, p143-150.
- Holland, H. D.: 1973, *Econ. Geol.* 68,1169-1172.
- Holland, H. D.: 1989A, *The Chemical Evolution of the Atmosphere and Oceans*, Princeton Univ. Press, p1-582.
- Holland, H. D.: 1989B, *The Chemical Evolution of the Atmosphere and Oceans*, Princeton University Press, Princeton, NJ, Chapter 4.
- Horowitz, N. H. & Miller, S. L.: 1962, *Fortschr. Chem. Org. Naturst.* 20,423.
- Ingmanson, D. E. & Dowler, M. J.: 1977, *Origins of Life* 8,221-224.
- Inoue, T., Joyce, G. F., Grzeskowiak, K., Orgel, L. E., Brown J. M., Reese C. B.: 1984, *J. Mol. Biol.* 178,669.

- Ito, K., Murata, T., and Ikeda, S.: 1975, *Bull. Nagoya Inst. Techn.* 27,209.
- Joe, H., Kuma, K., Paplawsky, W., Rea, B., & Arrhenius, G.: 1986, *Origins of Life* 16,369-370.
- Kapusta, S. & Hackerman, N.: 1983, *J. Electrochem. Soc.* 130,607-612.
- Kasting, J. F.: 1982, *J. Geophys. Res.* 87, 3091-3098.
- Kasting, J. F.: 1985, *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present* (ed. Sundquist, E. T. & Broecker, W. S.), American Geophysical Union, Washington, DC., p612-622.
- Kasting, J. F.: 1990, *Origins of Life* 20,199-231.
- Kasting, J. F., Holland, H. D, & Pinto, J. P.: 1985, *J. Geophys. Res.* 90,10,497-510.
- Kasting, J. F., Zahnle, K. J., Pinto, J. P., & Young, A. T.: 1989, *Org. Life Evol. Biosph.* 19,95-108.
- Kanemoto, M., Shiragami, T., Pac, C., & Yanagida, S.: 1992, *J. Phys. Chem.*, 96,3521-3526.
- Kim, J., Summers, D. P., & Frese Jr, K. W.: 1988, *J. Electroanal. Chem.*, 245,223.
- King, C. C.: 1990, *Origins of Life* 20,15-25.
- Koch, A. L.: 1985, *J. Mol. Evol.* 21,270-277.
- Kuhn, H. & Wasser, J.: 1981, *Angew. Chem. Int. Ed. Engl.* 20,500.
- Lalvani, S. B., Weston, A., & Masden, J. T.: 1990, *J. of Materials Sci.* 25,107-112.
- Liu, C. Y. & Bard, A. J.: 1989, *J. Phys. Chem.* 93, 7047-7048.
- Lund, C. R. F., Kubsh, J. E., Dumesic, J. A.: 1985, *Solid State Chem. Catal.*, 279,313-338.
- Mancinelli, R. L. & McKay, C. P.: 1988, *Origins of Life* 18,311-325.
- March J.: 1985, *Advanced Organic Chemistry* 3rd Ed., John Wiley & Sons, New York, 855-856 (and references therein).
- Mauzerall, D., Borowska, Z., & Zeilinski, I.: 1993, *Org. Life Evol. Biosph.*, 23,105-114.
- Miller, S. L. & Orgel, L. E.: 1974, *The Origins of Life on the Earth*, Prentice-Hall.
- Miller, S. L. & Van Trump, J. E.: 1981, *Origin of Life* (ed Y. Wolman), D. Reidel Publ. Comp., New York, p135-141.
- Mishra, K. K. and Osseo-Asare, K.: 1988, *J. Electrochem. Soc.* 135,2502-2509.
- Morikawa, K. & Ozaki, A.: 1971, *J. Catalysis* 23,97.
- Morrison, S. R.: 1977, *The Chemical Physics of Surfaces*, Plenum Press, New York.
- Morrison, S. R.: 1980, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, Plenum Press, New York.
- Morowitz, H. J.: 1992, *Metabolism Recapitulates Biogenesis, The Beginnings of Cellular Life*, Yale University Press.
- Morowitz, H. J., Heinz, B., & Deamer, D. W.: 1988, *Origins of Life* 18,281-287.
- National Research Council Committee on Planetary Biology and Chemical Evolution: 1990, *The Search for Life's Origins: Progress and Future Directions in Planetary Biology and Chemical Evolution*, National Academy Press, Washington, DC, 1990.
- Paik, W., Andersen, T. N., & Eyring, H.: 1969, *Electrochimica Acta* 14,1217-1232.
- Pinto, J. P., Gladstone, C. R., & Yung, Y. L.: 1980, *Science* 210,183.
- Rubin, M. B., Noyes, R. M., & Smith, K. W.: 1987, *J. Phys. Chem.* 91,1618-1622.

- Russell, P. G., Kovac, N., Srinivasan, S., Steinberg, M.: 1977, *J. Electrochem. Soc.* 124,1329-1337.
- Sakkopoulos, S.: 1986, *J. Appl. Phys.* 15,3540-3542.
- Schock, E. L.: 1992, *Origins of Life on Evol. of the Biosphere*, 22,67-108.
- Schrauzer, G. N., Strampach, N., Hui, L. N., Palmer, M. R., and Salehi, J.: 1983, *Proc. Natl. Acad. Sci.* 80,3873-3876.
- Summers, D. P., Leach, S., & Frese Jr., K. W.: 1986, *J. Electroanal. Chem.*, 205,219-221.
- Summers, D. P. & Frese Jr., K. W.: 1988, *Electrochemical Surface Science, Molecular Phenomena at Electrode Surfaces*, ACS Symposium Series No. 378, American Chemical Society, p. 518-527.
- Summers, D. P. & Frese Jr., K. W.: 1988, *Langmuir* 4,51-57.
- Summers, D. P. & Frese Jr., K. W.: 1988, *Langmuir*, 245,223.
- Summers, D. P. & Chang S.: 1993, *Nature* 365, 630-633.
- Stribling, R. E. & Miller, S. L.: 1987, *Origins of Life* 17,261-273.
- Teeter, T. E. & Van Rysselberghe, P.: 1954, *J. Chem. Phys.* 22,759.
- Turcotte, D. L.: 1980, *Earth Planet. Sci. Lett.* 48,53.
- Udupa, K. S., Subramanian, G. S., & Udupa, H. V. K.: 1971, *Electrochimica Acta* 16,1593-1598.
- Veizer, J.: 1978, *Precambrian Res.* 6,381-413.
- Veizer, J.: 1983, *Earth's Earliest Biosphere* (ed J. W. Schopf), Princeton Univ. Press, p240-259.
- von Kiedrowski, G.: 1986, *Angew. Chem. Int. Engl.* 25,932.
- Wächtershäuser, G.: 1988, *Microbiological Reviews* 52,452-484.
- Wächtershäuser, G.: 1988, *System. Appl. Microbiol.* 10,207-210.
- Wächtershäuser, G.: 1990, *Proc. Natl. Acad. Sci. USA* 87,200-204.
- Walker, J. C. G.: 1983, *Nature* 302, 518-519.
- Walker, J. C. G.: 1985, *Origins of Life* 16,117-127.
- Walker, J. C. G. & Brimblecombe, P.: 1985, *Precambrian. Res.* 28, 205-222.
- Weatherbee, G. D. & Bartholomew, C. H.: 1982, *J. Catalysis* 77,460-472.
- Wen, J., Pinto, J. P. and Yung, Y. L.: 1989, *J. Geophysical Research* 94,14957-14970.
- Windley, B. F. (ed): 1976, *The Early History of the Earth*, Wiley & Sons.
- Windley, B. F.: 1977, *The Evolving Continents*, Wiley & Sons.
- Wolery, T. J. & Sleep, N. H.: 1976, *J. of Geology* 84,249.
- Wood, B. J. & Vigo, D.: 1987, *Geochemica Cosmochemica Acta* 53,1277 (1989), d) J. F. Kasting *Precambrian Res.* 34,205-229.
- Yesodhara, E. & Graetzel, M.: 1983, *Helv. Chim. Acta* 66,2145-2153.
- Yung, Y. L. and McElroy, M. B.: 1979, *Science* 203,1002.
- Zafirious, O. C. & True M. B.: 1979, *Marine Chem.* 8, 9-32.
- Zahnle, K. J.: 1986, *J. Geophysical Research* 91,2819-2834.
- Zeilinski, W. S. & Orgel, L. E.: 1987, *Nature* 327,346.

David P. Summers and Sherwood Chang, "Experimental Results on the Prebiotic Fixation of Nitrogen Under a Neutral Atmosphere by Iron(II)", *Circumstellar Habitable Zones- Proceedings of the First International Conference* (Travis House Publications, 1996)."

David P. Summers and Narcinda Lerner, "Ammonia from Iron(II) Reduction of Nitrite and the Strecker Synthesis: Do Iron(II) and Cyanide Interfere with Each Other?", *Origins of Life and Evolution of the Biosphere*, Submitted.

David P. Summers, "Sources and Sinks for Ammonia and Nitrite on the Early Earth and the Reaction of Nitrite with Ammonia", *Origins of Life and Evolution of the Biosphere*, in preparation.